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Method for the Production of Thermostable, Color-Neutral, Antimony-Free Polyesters and Products Producing by Said Method

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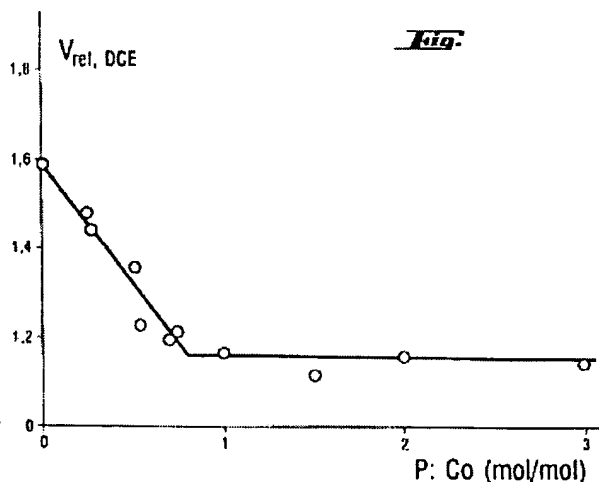
(54) [Title of the Invention]:

Method for the Production of Thermostable, Color-Neutral, Antimony-Free Polyesters and Products Producing by Said Method

(57) [Abstract]: The description is that of a method for the production of thermostable, color-neutral, antimony-free polyesters, [produced] by means of the esterification of aromatic dicarboxylic acids or transesterification of lower aliphatic esters of aromatic dicarboxylic acids with aliphatic diols and subsequent polycondensation, in which case an eventual trans-esterification is carried out in the presence of 20 to 120 ppm of a transesterification catalyst, relative to the catalyst metal, while, after completion of the esterification or transesterification, an amount equivalent to 100% of the employed transesterification catalyst and an amount equivalent of up to 99% of the cobalt to be employed is added to the esterification or transesterification batch in the form of

phosphoric acid, phosphorous acid and/or phosphonic acid or a derivative of the same, as a complexing agent, after which 80 ppm of cobalt is added to the batch in the form of a cobalt compound, while the polycondensation is carried out without the addition of antimony, in the presence of 1 to 10 ppm of titanium, which is added in the form of a titanium compound, and, optionally, in the presence of up to 1,000 ppm of organic compounds (pentaerythritol) that yield cross-linked structural components, and, optionally, up to 50 ppm of an optical brightener.

Polyesters that can be obtained in accordance with this method are also described.



Description

The present invention relates to a method for the production of thermostable, color-neutral, antimony-free polyesters, produced using a titanium polycondensation catalyst, said method being characterized by good reproducibility, exhibiting a very high polycondensation rate, even in cases of very small additions of titanium polycondensation catalyst, and which yields a considerable reduction of the thermal degradation and of the uncontrolled cross-linking of the formed polyesters; the invention also relates to the products producible in accordance with said method, which are characterized by excellent clarity and color neutrality.

Polyesters have gained very great importance in many areas of application. Saturated polyesters, in particular, are used on a large scale for the production of fiber materials, but also other types of molded articles, for example, beverage bottles. Very high requirements are imposed on the quality of the polyesters for a trouble-free processability of these polyesters by extrusion methods and for further use of the extruded products, for example, in the textile or beverage industry. It is required, in particular, that the processing and application properties of polyester types used for specific processes always be the same within very narrow limits. For processing by extrusion methods, for example, by melt spinning, it is of decisive importance that they always have a uniform molecular weight and an always reproducible molecular weight distribution, are free of gel fractions, and, if possible, have no tendency toward yellowing or thermal degradation. For further processing, no catalyst metals, if possible, should be released from the fiber material during dyeing processes, since these must be removed from the dye plant effluent and disposed of by costly purification operations.

During disposal or recycling of the used polyester products, no difficulty should occur from interfering components either.

The production of polyesters ordinarily occurs by esterification of aromatic dicarboxylic acids or transesterification of lower aliphatic esters of aromatic dicarboxylic acids with aliphatic diols and subsequent polycondensation until the molecular weight required for the intended use is reached.

An eventual transesterification is carried out in the presence of transesterification catalysts that must be deactivated after the conclusion of the transesterification by means of the addition of complexing agents. Phosphoric acid, phosphorous acid and/or phosphonic acids or their derivatives are generally used as complexing agents.

After esterification or transesterification, polycondensation to the desired molecular weight occurs, which is also carried out in the presence of an appropriate catalyst. Antimony compounds, generally antimony trioxide, have gained acceptance in the large-scale production as polycondensation catalysts.

It can happen in this context that a portion of the antimony compound is reduced to antimony metal by reducing agents, which leads to graying of the polyester. Insufficient clarity and a non-neutral color tone are the result.

The relatively high content of antimony compounds in polyesters is also seen as a disadvantage, since it makes production more costly. There is the additional possibility that antimony compounds will be released during further processing methods, for example, during dyeing. The relatively high content of antimony compounds has a negative effect on the spinning process, in addition to the formation of antimony deposits.

Proposals have therefore already been made to eliminate the disadvantages of the described production method.

Thus, it is known that the color tone of polyesters can be improved by adding cobalt compounds and/or optical brighteners. It is also known that titanium compounds can be used as polycondensation catalysts, instead of antimony compounds.

A method for the production of polyesters, in which a cobalt compound is added to improve the color tone of the polyester, which requires that said cobalt compound, like the transesterification catalyst, must be complexed prior to the beginning of the polycondensation, and in which the polycondensation is carried out in the presence of a titanium compound, is known from various publications, for example, US-A-3,962,189, JP-PS-28006 (1979), JP-PS-123311 (1976), JP-PS-43564 (1979), JP-PS-111985 (1980), or JP-PS-280048 (1989).

The amount of complexing agent used to complex the cobalt additive, according to these publications, should lie in the range from 0.5 to 7.5 mol per mol of cobalt compound.

According to JP-PS-28006, a P/Co ratio of 0.5 to 1.5 is used, in JP-PS-111985 from 0.7 to 3, and in JP-PS-280048 from 0.5 to 7.5 [mol/mol].

This known method has the considerable advantage that all the disadvantages associated with the use of antimony compounds are eliminated and that color-neutral and clear polyesters that are suitable for demanding processing methods and applications can actually be produced with it.

However, a disadvantage of this known process is that its reproducibility leaves much to be desired.

Occasionally, it is not the desired products that are obtained, but disturbances in the polycondensation reaction occur, and the required molecular weights are not reached and during lengthening of the polycondensation time that is deemed necessary, yellowing of the polyester occurs and the formation of gel fractions occur by means of an uncontrolled crosslinking, along with thermal sensitivity of the product, which seriously compromises further processing.

The advantages that the method offers are therefore not always realized.

It has now been found, surprisingly, that thermostable, color-neutral, antimony-free polyesters can be produced in a constantly reproducible fashion by means of the esterification of aromatic dicarboxylic acids or the transesterification of lower aliphatic esters of aromatic dicarboxylic acids with aliphatic diols and subsequent polycondensation, when

an eventual esterification is carried out in the presence of 20 to 120 ppm, relative to the catalyst metal, of a transesterification catalyst, preferably of manganese in the form of a manganese compound,

after completion of the esterification or transesterification, an amount equivalent to 100% of the employed transesterification catalyst and an amount equivalent of up to 99% of the cobalt to be employed is added to the esterification or transesterification batch in the form of phosphoric acid, phosphorous acid and/or phosphonic acid or a derivative of the same, as a complexing agent, after which 80 ppm of cobalt is added to the batch in the form of a cobalt compound,

while the polycondensation is carried out without the addition of antimony, in the presence of 1 to 10 ppm of titanium, which is added in the form of a titanium compound, and, optionally, in the presence

of up to 1,000 ppm of organic compounds that yield cross-linked structural components,

and, optionally, up to 50 ppm of an optical brightener.

Appropriate transesterification catalysts are known from the literature. For example, compounds of metals of groups Ia (for example, Li, Na, K), group IIa (for example, Mg, Ca) and group VIIa (for example, Mn) of the periodic system, are suitable for the method according to the invention, especially those having a certain solubility in the transesterification batch, for example like salts of organic acids. Salts of group VIIa, especially manganese, with lower aliphatic carboxylic acids, especially acetic acid, are preferred.

A preferred embodiment of the method according to the invention therefore consists of running the eventual transesterification in the presence of 20 to 120 ppm of manganese (calculated as metal) in the form of a manganese compound, especially manganese acetate.

The cobalt compound added to improve the color tone of the polyester is expediently also a salt of cobalt with an organic acid, for example, with acetic acid or adipic acid.

The minimum amount of cobalt compound is dependent on the degree of color shift required in each individual case in order to achieve a neutral color tone. If optical brighteners are additionally used for a color correction, the amount of cobalt compound can naturally be reduced. The required amount of cobalt additive, as mentioned above, is generally maximally 50 ppm (calculated as metal), always in reference to the weight of the polyester.

20 to 40 ppm cobalt is preferably added to the batch in the form of a cobalt compound, i.e., an amount of cobalt compound that corresponds to an amount of 20 to 40 ppm of free cobalt is added.

As in the case of the conventional methods, the transesterification catalyst is also inactivated in the method according to the invention before the beginning of polycondensation by adding a complexing agent, because otherwise polycondensation is hampered, i.e., the required high molecular weights of the polyester cannot be reached and the obtained polyester also has increased sensitivity to thermal loading. In some cases, the cobalt compounds added before the polycondensation have also been complexed in order to improve the thermal stability of the produced polyesters.

For the method according to the invention, it is now essential that in no case must the entire added amount of cobalt compound be inactivated, but instead 1 to 10% of the added cobalt compound must remain uncomplexed.

The amount of complexing agent is therefore calculated so that the transesterification catalyst is 100% deactivated by complexing, but only 90 to 99% of the cobalt compound is complexed.

If the complexing capacity of the complexing agent is precisely known, one can simply use 90 to 99% of the amount of complexing agent equivalent to the amount of cobalt. However, it is generally more expedient to determine the required amount of complexing agent by preliminary experiments. For this purpose, some trial batches of the polycondensation batch, all of which have the same composition as a planned main batch, are mixed with about 80 to 120% of the theoretically required amount of complexing agent and then subjected to polycondensation under the same conditions.

On conclusion of the polycondensation reaction, the viscosity reached by all batches (i.e., the obtained molecular weight) is determined.

The results of such a series of preliminary experiments are shown in the figure. The achieved viscosities are plotted in said figure on a coordinate system versus the ratio of complexing agent to cobalt compound (for example, the P/Co ratio).

It is apparent that only low viscosities, i.e., low molecular weights, can be achieved at an unduly high P/Co ratio. Below a certain limit of the P/Co ratio, the achieved molecular weights increase.

The intersection point between the flat and rising parts of the curve marks the equivalent P/Co ratio.

Up to 99% of the amount of complexing agent so determined is then added to the main batch.

It is particularly advantageous if 100% of the amount equivalent to the amount of transesterification catalyst and 90 to 99% of the amount equivalent to the employed cobalt are added to the esterification or transesterification batch in the form of phosphoric acid, phosphorous acid and/or phosphonic acids or a derivative thereof after conclusion of the esterification or transesterification.

The measure of only partially deactivating the added cobalt compound surprisingly leads to a drastic improvement in the reproducibility of the method and a very high rate of polycondensation is obtained even with a very limited addition of the titanium polycondensation catalyst, along with a significant reduction of the thermal degradation and the uncontrolled crosslinking of the formed polyester with the result that no yellowing and no gel formation occur. In running the reaction, one therefore also gets by with smaller amounts of brightening [*or: fining - translator*] additives and achieves trouble-free processability. The obtained polyesters meet the highest quality requirements in terms of clarity and color neutrality.

All compounds known as complexing agents and deactivators for transesterification catalysts are suitable, in principle, as complexing agents for the method according to the invention. Phosphorous-containing compounds, like phosphoric acid, polyphosphoric acid, phosphorous acid and phosphonic acids and their derivatives, have been shown to be particularly suitable. Special examples of phosphoric acid derivative are the "PHM esters". These are mixtures of alkoxyated alkylhydroxyalkyl-phosphoric acid esters with the formula I or phosphonic acid esters of the formula II



in which the groups R^1 are the same or different alkyl, hydroxyalkyl or alkoxyated hydroxyalkyl groups.



in which R^2 , R^3 and R^4 are alkyl groups.

Titanium compounds are used as polycondensation catalysts in the method according to the invention. All titanium compounds already described for this purpose are suitable, in principle, especially potassium titanyl oxalate or titanium isopropylate.

It is particularly preferred to run polycondensation without the addition of antimony in the presence of 1 to 10 ppm of titanium to an intrinsic viscosity (IV), measured in dichloroacetic acid at 25°C, from 0.4 to 0.9 dL/g, preferably from 0.5 to 0.7 dL/g, and to a carboxyl group

concentration from 10 to 50 mmol/kg, preferably 10 to 40 mmol/kg, in the melt, and then to the desired final viscosity in the solid phase.

The final viscosity of the polyesters according to the invention should lie in the range from 0.7 to 2.0 dL/g, preferably from 0.7 to 1.5 dL/g, measured under the conditions just mentioned. The polycondensation time and polycondensation temperature are regulated in known fashion, so that the desired final viscosity is reached.

Polycondensation is generally run as is usual in polyester production, depending on the type of polyester, at a temperature from 260 to 350°C, preferably under an inert gas, for example, under nitrogen, and/or under reduced pressure, which lies in the range from 0.2 to 10 mbar, preferably from 0.4 to 5 mbar.

To set specific polyester properties, for example, melt viscosity, it can be desired to produce a defined degree of crosslinking.

For this purpose, polycondensation is run without the addition of antimony in the presence of 2-8 ppm of titanium and in the presence of up to 1,000 ppm, preferably 100 to 500 ppm of compounds that yield crosslinking structural groups (cross-linking agents).

Compounds that have at least three functional groups capable of ester formation serve as cross-linking agents. Functional groups capable of ester formation include the OH group, the carboxyl group, alkoxy carbonyl, especially lower alkoxy carbonyl, the carboxylic acid anhydride group and reactive groups derived from the aforementioned groups. Examples of common cross-linking agents are pentaerythritol, trimethylol propane, trimellitic acid, trimesic acid, pyromellitic acid, etc.

For further improvement of the color tone of the polyester and to save a portion of the cobalt, it has also proven to be expedient to run the polycondensation without the addition of antimony in the presence of up to 50 ppm, preferably 5 to 25 ppm, of an optical brightener.

The chemical composition of the polyesters is naturally of greatest significance in terms of their properties. For the production of polyesters that are suitable for the aforementioned applications, under the aforementioned conditions for the method according to the invention

80 to 100 mol% of aromatic dicarboxylic acids of the formula III



or their lower aliphatic esters, and 0 to 20 mol% of aromatic hydroxycarboxylic acids of the formula IV



or their lower aliphatic esters are esterified or transesterified with diols of the formula (V)



in which

X, in reference to the total amount of di- and hydroxycarboxylic acid, denotes more than 80 mol% of the aromatic groups with 5 to 16, preferably 6 to 12 carbon atoms and maximally 20 mol% of the aliphatic groups with 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms,

X^1 , denotes the p-phenylene group,

Y, in reference to the total amount of transesterified or esterified diols, denotes at least 80 mol% of the alkylene or polymethylene groups with 2 to 4 carbon atoms or cycloalkane or dimethylene cycloalkane groups with 6 to 10 carbon atoms and

maximally 20 mol% of the straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8 carbon atoms or groups of the formula $(\text{C}_2\text{H}_4\text{-O})_n\text{-C}_2\text{H}_4\text{-}$, in which n is whole number from 1 to 40, in which case $n = 1$ or 2 is preferred for fractions up to 20 mol%, and groups with $n = 10$ to 40 are preferably present only in fractions of less than 5 mol%.

It is particularly preferred to choose the starting materials so that

X, in reference to the total amount of di- and hydroxycarboxylic acids, denotes 90 to 100 mol% of the p-phenylene groups, 0 to 7 mol% of the m-phenylene groups and 0 to 5 mol% of the aliphatic groups with 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms, and

X^1 , denotes the p-phenylene group,

Y, in reference to the total amount of transesterified or esterified diols, denotes at least 90 mol% of the alkylene or polymethylene groups with 2 to 4 carbon atoms, or cycloalkane or dimethylene cycloalkane groups with 6 to 10 carbon atoms, and

maximally 10 mol% of the straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8 carbon atoms, or groups of the formula $-(\text{C}_2\text{H}_4\text{-O})_n\text{-C}_2\text{H}_4\text{-}$ in which n stands for the numbers 1 or 2.

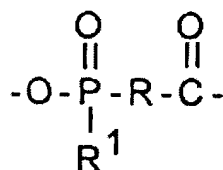
It is particularly preferred not to use a hydroxycarboxylic acid of the formula IV in the method according to the invention and to choose the dicarboxylic acid component of formula III, so that X, in reference to the total amount of di- and hydroxycarboxylic acids, denotes 93 to 99 mol%, preferably 95 to 98 mol% of the p-phenylene groups, [and] 1 to 7 mol%, preferably 2 to 5 mol% of the m-phenylene groups.

The aromatic groups, which are represented by X and X^1 , can be unsubstituted or, if specific properties of the polyester are to be modified, can carry one or two substituents.

The groups preferably are mostly unsubstituted, i.e., no more than 10 mol% of the aromatic groups carry substituents. The precise percentage of substituted groups is established according to the effect to be achieved.

The methyl group and sulfonic acid group are preferably considered as substituents.

In addition to the aforementioned starting materials, up to 10 mol%, preferably up to 7 mol%, of other co-condensable compounds can be condensed in the polyester, if specific special properties are desired. For example, poorly flammable polyesters can be produced by means of the method according to the invention, if 1 to 10 mol% of the compounds known from DE-C-23 46 787 and 24 54 189, in reference to the total condensed dicarboxylic acids and optionally hydroxycarboxylic acids, are condensed in the polyester, which yields polyester structural groups of the formula VI



(VI)

in which

- R denotes a saturated open-chain or cyclic alkylene, arylene or aralkylene group, preferably alkanediyl with 2 to 6 carbon atoms, cycloalkanediyl with 6 carbon atoms, methylene-phenyl or phenylene, especially ethylene, and
- R¹ denotes an alkyl group with up to 6 carbon atoms or an aryl or aralkyl group, preferably alkyl with 1 to 6 carbon atoms, or aryl or aralkyl with 6 to 7 carbon atoms, especially methyl, ethyl, phenyl or benzyl.

Up to 10 wt.% of modifying additives, fillers, pigments, dyes, antioxidants, hydrolysis, light and temperature stabilizers and/or processing auxiliaries can be added to the esterification, transesterification or polycondensation batches, if these additives do not inhibit the titanium catalyst.

In particular, the addition of up to 10 wt.%, preferably up to 5 wt.% of polyester stabilizers that protect the polyester fraction of the mixture against hydrolysis and thermal degradation is preferred in the method according to the invention. Those compounds that can react with terminal carboxyl groups of the polyester to nonacid terminal groups, like glycidyl ethers, ketene imines, aziridines, isocyanates, are particularly advantageous as stabilizers.

Carbodiimides and polycarbodiimides are particularly advantageous as stabilizers, especially if used in combination with each other.

The polyesters produced according to the described method that are based on aromatic dicarboxylic acids and aliphatic diols, which are characterized by the fact that, in the unmatted state, among their color number components

a* lies in the range from -3 to +3, preferably from -2 to +2,

b* lies in the range from -6 to +6, preferably -3.5 to +3.5

and

L* lies in the range from 55 to 75, preferably from 60 to 70,

also constitute a subject matter of the invention.

The polyester according to the invention is also characterized by the fact that it is free of antimony

and contains

1 to 10 ppm of titanium (calculated as metal),

20 to 120 ppm of a transesterification catalyst metal in the form of catalytically inactive complexes with phosphoric acid,

phosphorous acid and/or phosphonic acids or a derivative thereof, and

0 to 80 ppm of cobalt (calculated as metal), which is present partially in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or a derivative thereof

and optionally up to 50 ppm of an optical brightener.

The polyester according to the invention is preferably free of antimony and contains

2 to 8 ppm of titanium (calculated as metal),

50 to 90 ppm of manganese (calculated as metal) in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or a derivative thereof,

and 20 to 40 ppm of cobalt, which is present partially in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or a derivative thereof and optionally up to 25 ppm of an optical brightener.

It is also preferred that 90 to 99% of the cobalt be present in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or a derivative thereof and/or that it contains 5 to 25 ppm of an optical brightener.

The catalytically inactive complexes of the transesterification catalyst, preferably of manganese, and of cobalt, can contain, in principle, all complexing agents known for inactivation of these metals. Catalytically inactive complexes of the transesterification catalyst are preferred,

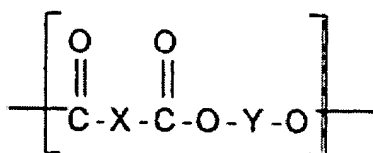
especially of manganese and cobalt, with phosphoric acid, polyphosphoric acid, or especially phosphorous acid or a derivative thereof, especially an ester of these acids.

The structure of the polyester chain is naturally also of special significance for the overall technical properties. It can be stated purely qualitatively that it is constructed from the structural groups common in known fiber-forming polyesters.

They primarily, i.e., to at least 80 mol%, consist of components that are derived from aromatic dicarboxylic acids and aliphatic diols. Common aromatic dicarboxylic acid components are the divalent groups of benzene-dicarboxylic acids, especially terephthalic acid and isophthalic acid; common diols have 2 to 4 carbon atoms, in which case ethylene glycol is particularly suitable. Modified polyesters preferably contain at least 80 mol% of ethylene terephthalate units. The remaining 20 mol% are then constructed from dicarboxylic acid units and glycol units that act as so-called modifying agents and which permit one skilled in the art to deliberately influence the physical and chemical properties of the products produced from the polyesters, like filaments and packaging materials (for example, beverage bottles). Examples of such dicarboxylic acid units are groups of isophthalic acids or of aliphatic dicarboxylic acids, like glutaric acid, adipic acid or sebacic acid. Examples of modifying diol groups are those from long-chained diols, like propanediol or butanediol, of di- or triethylene glycol or, if present in limited amounts, of polyglycol with a molecular weight of about 500-2,000.

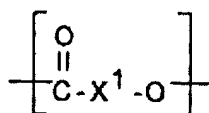
In particular, polyesters according to the invention, whose polymer chains are constructed from

80 to 100 mol% of structural groups of the formula VI



(VI)

and 20 to 0 mol% of structural groups of formula VII



(VII)

are preferred, in which

X denotes more than 80 mol% of the aromatic groups with 5 to 16, preferably 6 to 12 carbon atoms and maximally 20 mol% of the aliphatic groups with 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms,

X¹ denotes the p-phenylene group,

Y denotes at least 80 mol% of the alkylene or polymethylene groups with 2 to 4 carbon atoms or cycloalkane or dimethylene cycloalkane groups with 6 to 10 carbon atoms and maximally 20 mol% of the straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8, carbon atoms or groups with the formula $-(C_2H_4-O)_n-C_2H_4-$, in which n is whole number from 1 to 40, in which case n = 1 or 2 is preferred for fractions up to 20 mol%, and groups with n = 10 to 40 are preferably present only in fractions of less than 5 mol%.

Polyesters according to the invention that are particularly preferred are those that consist of structural groups of formula IV, in which

X denotes up to 90 to 100 mol% of the p-phenylene groups, up to 0 to 7 mol% of the m-phenylene groups and up to 0 to 5 mol% of the aliphatic groups of 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms, and

Y denotes at least 90 mol% of the alkylene or polymethylene groups with 2 to 4 carbon atoms or cycloalkane or dimethylene cycloalkane groups with 6 to 10 carbon atoms and maximally 10 mol% of the straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8, carbon atoms or groups with the formula $-(C_2H_4-O)_n-C_2H_4-$, in which n stands for the numbers 1 or 2.

In particular, those polyesters according to the invention that consist of structural groups of formula IV, in which

X denotes up to 93 to 99 mol% of the p-phenylene groups and up to 1 to 7 mol% of the m-phenylene groups are particularly preferred.

It is often expedient to adjust a defined degree of crosslinking of the polyester. In these cases, it is preferred that the polyester contains up to 1,000 ppm of the aforementioned crosslinking structural groups.

The polyesters according to the invention that are produced by melt polycondensation expediently have an intrinsic viscosity (IV) from 0.600 to 0.900, measured in dichloroacetic acid at 25°C.

Polyesters having structural groups of formula VII preferably contain 70 to 100 mol%, especially 85 to 100 mol%, of the structural groups of formula VI and 0 to 30 mol%, especially 0 to 15 mol%, of the structural groups of formula VII.

The aromatic groups, which are represented by X, can all be the same or different.

In particular, the aforementioned structural groups represented by X, which form the polyester chain to at least 80 mol%, can be present individually or mixed in the polyester chain.

It is preferred if at least 80% of the polyester chain is formed from only one or two individuals from the groups mentioned for these main components. Any desired additional modification of the polyester chain then preferably occurs by means of other structural groups in the context of the definition that was given for the structural groups represented by X that are present to maximally 20 mol%.

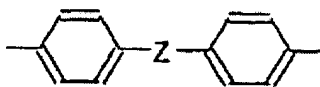
Thus, the at least 80 wt.% of the aromatic groups can all be 1,4-phenylene groups or they can consist of 1,4- and 1,3-phenylene groups in a molar ratio from 95:5 to 99:1 or of 2,6-naphthylene groups and biphenyl-4,4'-diyl groups in a molar ratio from 4:6 to 6:4. Polyesters, in which X denotes at least 95 mol% of the aromatic and maximally 5 mol% of the aliphatic groups, but especially those in which X exclusively stands for aromatic groups, are preferred.

The groups, which are represented by Y, can also all be the same or different within the context of the given definition. In particular, the aforementioned structural groups represented by Y, which form at least 80 mol% of the polyester chain, can be present individually or mixed in the polyester chain. It is preferred if the at least 80 mol% of the polyester chain are formed by only one or two individuals from the groups mentioned for these main components.

Any desired additional modifications of the polyester chain then preferably occurs by means of other structural groups in the context of the definition given for the structural groups represented by Y that are present to maximally 20 mol%. They can be at least 80 wt.% of the aliphatic groups, for example, all ethylene groups, or can consist of ethylene and 1,4-dimethylene cyclohexane groups in a molar ratio from 10:1 to 1:10.

Polyesters, in which Y is at least 95 mol% of the ethylene groups, are particularly preferred.

Preferred aromatic groups, which are represented by X, are 1,4- and 1,3-phenylene. Suitable groups, however, are also 1,4-, 1,5-, 1,8-, 2,6- and 2,7-naphthylene, 4,4'-biphenylene, furylene and groups of the formula VI



(VI)

in which Z denotes polymethylene or alkylene with 1 to 4 carbon atoms, $-\text{SO}_2-$, $-\text{COO}-$, $-\text{O}-$ or $-\text{S}-$.

The aromatic groups, which are represented by X, can, in turn, carry one or two additional substituents. However, in this case, it is preferred that only a fraction of up to 15%, especially up to 7%, of the aromatic groups that are present be substituted. The substituted aromatic groups preferably carry only one substituent each. Particularly preferred substituents

are alkyl with 1 to 4 carbon atoms; alkoxy with 1 to 4 carbon atoms, chlorine and the sulfo group.

Groups that are derived from aliphatic dicarboxylic acids and aromatic groups that furnish angled chains, for example, isophthalic acid groups, or which have bulkier aromatic nuclei, like the naphthalene nucleus, as well as the longer-chain structural groups standing for Y, are incorporated in the polyester chain, in particular, if modification of the properties of the polyester is desired. Polyesters that contain less than 7% of these modifying components are preferred.

To achieve special use properties, incorporation, for example, of components containing sulfo groups (for example, sulfoisophthalic acid) in the polyester is used, which acquires an affinity to basic dyes on this account, or the incorporation of structural groups of the aforementioned formula VI is used, which leads to poorly flammable polyesters.

Example 1a

9.75 kg of dimethyl terephthalate, 0.25 kg of dimethyl isophthalate, 6 kg of ethylene glycol and 3 g of manganese acetate $\cdot 4 \text{H}_2\text{O}$ (68 ppm manganese, in reference to polyester) are fed into a transesterification reactor and the mixture is heated during agitation under nitrogen as a protective gas to 140°C. The reaction temperature is raised to 230°C over 4 hours and the split-off methanol and ethylene glycol excess distilled off.

The molten reaction product is transferred to a polycondensation vessel, mixed with 1.65 g (165 ppm) of H_3PO_3 as complexing agent and 1.27 g (127 ppm) of cobalt acetate (corresponding to 30 ppm Co) and agitated for 10 to 15 minutes at 230°C. 0.27 g (27 ppm) of potassium titanyloxalate (corresponding to 3.6 ppm Ti) is then added and the batch agitated under nitrogen at 240°C, during which ethylene glycol is distilled off under low vacuum.

The internal pressure is then reduced to 1.13 mbar over an hour and the temperature of the melt then increased from 240 to 270°C. Over another half-hour, the temperature is raised to 280°C and agitation continued until a sample of the melt has a specific solution viscosity of 0.83, measured in a solution of 1 g of melt in 100 mL dichloroacetic acid at 25°C.

As an alternative and more conveniently, the polycondensation can also be continued to a specified melt viscosity, if the melt viscosity that corresponds to a solution viscosity of 0.83 was determined in preliminary experiments at 280°C.

The melt is cooled and processed in the usual manner to pellets with a diameter of 2 to 3 mm. The polyester so obtained has the following characteristics:

Content of carboxyl groups (mmol/kg):	12
Content of diethylene glycol (%):	0.5
Color indices: $L^* = 63.44$; $a^* = -0.62$;	$b^* = 3.09$

The polyester so produced can be further condensed by solids condensation. For this purpose, the pellets produced above are heated in the usual manner during slow mixing in a vacuum or under nitrogen for 17 hours to 220°C. A polyester with a specific viscosity of 1.014, as measured above, is obtained.

Examples 1b to 1l

The above example was repeated a number of times in the batchwise method described in example 1a (examples 1j to 1l) or similarly in a continuous operation (examples 1b to 1i), in which the amount of cobalt additive, the type and amount of complexing agent, as well as the type and amount of titanium catalyst, were modified and, in some cases, a commercial optical brightener ([®]HOSTALUX KS from Hoechst AG) or a cross-linking agent (pentaerythritol) was additionally added. During melt polycondensation, different pressures and varied reaction times were used and the condensation time and temperature were varied during solids condensation.

The composition of the batches and the reaction condition, if varied, the color indices, as well as the achieved specific viscosity and content of carboxylic acid groups and diglycol in the polyesters, are provided in the following tables 1 and 2.

The abbreviations used in the table have the following meanings:

KTi = potassium titanyloxalate; Tiip = isopropyl titanate $\text{Co}(\text{ACO})_2 \cdot 4 \text{H}_2\text{O}$ = cobalt acetate tetrahydrate

PO_3 = phosphorous acid; PO_4 = phosphoric acid

PPA = polyphosphoric acid; PHM = PHM ester

HLX = [®]HOSTALUX KS; Penta = Pentaerythritol

SV = specific viscosity

[COOH] carboxyl terminal group concentration; DEG = concentration of diethylene glycol

All ppm data refer to the amount of polyester that can theoretically be obtained in the batch. If the additive is a metal compound (for example, catalyst), the name of the compound abbreviation means that the ppm amount denotes the amount of compound, if the metal symbol is stated, the ppm amount denotes the amount of metal contained in the additive.

Table 1

Example No.	Polycondensation catalyst		Cobalt compound		Complexing agent		Additional additives ^a	
	Type	Amount (ppm)	Type	Amount (ppm) total	Amount (%) free	Type	Amount (ppm) total	Type
1b	KTi	27	Co(Ac) ₂	84	0	PO ₃	150	-
1c	KTi	27	Co(Ac) ₂	84	0	PO ₃	150	HLUX
1d	KTi	27	Co(Ac) ₂	127	0	PO ₃	165	HLUX
1e	KTi	27	Co(Ac) ₂	127	0	PO ₃	165	Penta
1f	KTi	54	Co(Ac) ₂	127	0	PO ₃	165	-
1g	KTi	54	Co(Ac) ₂	169	0	PO ₃	189	-
1h	KTi	27	Co(Ac) ₂	127	100	PO ₃	121	-
1i	Sb ₂ O ₃	395	-	-	-	PO ₃	121	-
1j	KTi	45	Co(Ac) ₂	135	10	PO ₃	140	Penta
1k	KTi	27	Co(Ac) ₂	127	100	PO ₃	121	-
1l	Sb ₂ O ₃	390	-	-	-	PO ₃	-	-

Table 2

Example No.	Melt condensation		SV	(COOH) (mmol/kg)	DEG (%)	Color indices			Solids condensation		SV
	Pressure (mbar)	Time (min)				L*	a*	b*	Time (h)	Temp (°C)	
1b	1.1	-	0.851	11	0.47	65.76	-1.19	5.89	14	220	1.048
1c	0.9	-	0.835	15	0.48	66.57	-0.62	4.07	16	220	1.057
1d	0.8	-	0.835	13	0.48	64.95	0.12	0.98	18.5	220	1.019
1e	1.1	-	0.826	10	0.53	67.30	0.12	0.77	14	220	1.032
1f	1.6	-	0.848	12	0.55	66.19	-0.94	4.92	10.5	220	1.063
1g	1.0	-	0.840	12	0.50	64.37	0.27	-0.11	16	220	1.000
1h	1.3	-	0.846	17	0.53	66.28	-0.03	2.34	14	220	1.055
1i	1.6	-	0.829	13	0.55	64.07	-2.31	7.27	9.25	220	1.038
1j	0.8	141	0.832	15	0.74	62.75	0.86	2.65	12	225	1.048
1k	0.8	189	0.853	9	0.72	66.35	-0.30	-0.19	12	220	1.134
1j	0.8	184	0.834	11	0.63	64.64	-2.51	4.16	12	225	1.053

Example 2

The following embodiment explains the production of a polyester by means of a direct esterification:

An esterification reactor is fed with 8.29 kg of terephthalic acid, 0.124 kg of isophthalic acid and 4.0 kg of ethylene glycol and the mixture is heated during agitation under nitrogen as a protective gas under a pressure of 3.2 bar, so that the split-off water is distilled off.

When water cleavage is ended, the molten reaction product is transferred to a polycondensation vessel, mixed with 0.35 g (32 ppm) of H_3PO_3 as the complexing agent and 1.47 g (135 ppm) of cobalt acetate tetrahydrate (corresponds to 32 ppm Co).

0.49 g (45 ppm) of potassium titanyl oxalate (corresponds to 6.1 ppm Ti) is then added and the batch agitated under nitrogen at 240°C, during which ethylene glycol is distilled off under low vacuum.

The internal pressure is then reduced to 1.13 mbar over an hour and the temperature of the melt raised from 240 to 270°C. Over another half-hour, the temperature is then raised to 280°C and agitation continued until a sample of the melt has a specific solution viscosity of 0.83, measured in a solution of 1 g of the melt in 100 mL dichloroacetic acid at 25°C.

The melt is cooled and processed in the usual manner to pellets with a diameter of 2 to 3 mm.

The polyester so obtained has the following characteristics:

Content of carboxyl groups (mmol/kg):	13
Content of diethylene glycol (%):	1.19
Color indices: $L^* = 63.6$; $a^* = 1.90$;	$b^* = -1.5$

The polyester so produced can be further condensed by solids condensation.

For this purpose, the pellets prepared above, during slow mixing, are heated under nitrogen or in vacuum for 9.5 hours to 220°C. A polyester with a specific viscosity of 1.087, as measured above, is obtained.

Additional polyesters can be produced in analogous fashion, by means of the conditions apparent from Tables 3 and 4.. The products have the properties shown in Table 4.

Table 3

Example No.	Polycondensation catalyst		Cobalt compound			Complexing agent		Additives	
	Type	Amount (ppm)	Type	Amount (ppm)	% free	Type	Amount (ppm)	Type	Amount (ppm)
2b	Sb ₂ O ₃	298	-	-	-	H ₃ PO ₃	32	Penta	200
2c	KTi	45	Co(Ac) ₂	84	100	-	-	Penta	200
2d	KTi	45	Co(Ac) ₂	135	25	H ₃ PO ₃	32	Penta	200

Table 4

Example No.	Melt condensation pressure (mbar)	SV	-COOH (mmol/kg)	DEG (%)	Color indices		
					L*	a*	b*
2b	2.75	0.812	20	1.51	62.8	-1.8	5.2
2c	4.7	0.814	21	1.49	63.6	0.5	4.7
2d	2.35	0.823	12	1.36	64.6	1.7	0.9

Claims

1. A method for the production of thermostable, color-neutral, antimony-free polyesters, [produced] by means of the esterification of aromatic dicarboxylic acids or transesterification of lower aliphatic esters of aromatic dicarboxylic acids with aliphatic diols and subsequent polycondensation, characterized by the fact that an eventual transesterification is carried out in the presence of 20 to 120 ppm of a transesterification catalyst, relative to the catalyst metal, while, after completion of the esterification or transesterification, an amount equivalent to 100% of the employed transesterification catalyst and an amount equivalent of up to 99% of the cobalt to be employed is added to the esterification or transesterification batch in the form of phosphoric acid, phosphorous acid and/or phosphonic acid or a derivative of the same, as a complexing agent, after which 80 ppm of cobalt is added to the batch in the form of a cobalt compound, while the polycondensation is carried out without the addition of antimony, in the presence of 1 to 10 ppm of titanium, which is added in the form of a titanium compound, and, optionally, in the presence of up to 1,000 ppm of organic compounds (pentaerythritol) that yield cross-linked structural components, and, optionally, up to 50 ppm of an optical brightener.
2. The method according to Claim 1, characterized by the fact that after completion of the esterification or transesterification, an amount equivalent to 100% of the employed transesterification catalyst and an amount equivalent of 90 to 99% of the cobalt to be employed is added to the esterification or transesterification batch in the form of phosphoric acid, phosphorous acid and/or phosphonic acid or a derivative of the same, as a complexing agent.
3. The method according to one of the Claims 1 and 2, characterized by the fact that the polycondensation is carried out without an addition of antimony in the presence of 1 to 10 ppm of titanium up to an intrinsic viscosity (IV) of 0.4 to 0.9 dL/g, measured in dichloroacetic acid at 25°C, and up to a carboxyl group concentration of 10 to 50 mmol/kg in the melt, after which the polycondensation is continued to the desired final viscosity in the solid phase.
4. The method according to one of the Claims 1 to 3, characterized by the fact that 20 to 40 ppm of cobalt, in the form of a cobalt compound, are added to the batch.

5. The method according to one of the Claims 1 to 4, characterized by the fact that the polycondensation without the addition of antimony is carried out in the presence of 2-8 ppm of titanium and optionally in the presence of up to 1,000 ppm of organic compounds that yield cross-linking structural components.
6. The method according to one of the Claims 1 to 5, characterized by the fact that the polycondensation is carried out in the presence of 100 to 500 ppm of organic compounds that yield cross-linking structural components.
7. The method according to one of the Claims 1 to 6, characterized by the fact that the polycondensation without the addition of antimony is carried out in the presence of up to 25 ppm of an optical brightener.
8. The method according to one of the Claims 1 to 7, by means of the esterification of aromatic dicarboxylic acids or hydroxycarboxylic acids, or transesterification of lower aliphatic esters of aromatic dicarboxylic acids or hydroxycarboxylic acids with aliphatic diols and subsequent polycondensation, characterized by the fact that 80 to 100 mol% of aromatic dicarboxylic acids of formula III



or their lower aliphatic esters, and

0 to 20 mol% of aromatic hydroxycarboxylic acids of the formula IV



or their lower aliphatic esters are esterified or transesterified with diols of the formula (V)



in which

X, in reference to the total amount of di- and hydroxycarboxylic acid, denotes more than 80 mol% of the aromatic groups with 5 to 16, preferably 6 to 12 carbon atoms and maximally 20 mol% of the aliphatic groups with 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms,

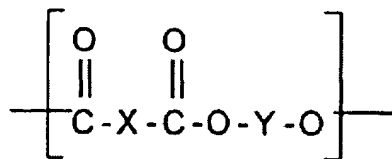
X^1 , denotes the p-phenylene group,

Y, in reference to the total amount of transesterified or esterified diols, denotes at least 80 mol% of the alkylene or polymethylene groups with 2 to 4 carbon atoms or cycloalkane or dimethylene cycloalkane groups with 6 to 10 carbon atoms and maximally 20 mol% of the straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8 carbon atoms or groups of the formula $(C_2H_4-O)_n-C_2H_4-$, in which n is whole number from 1 to 40, in which case $n = 1$ or 2 is preferred for fractions up to 20 mol%, and groups with $n = 10$ to 40 are preferably present only in fractions of less than 5 mol%.

9. The method according to one of the Claims 1 to 8, characterized by the fact
 X, in reference to the total amount of di- and hydroxycarboxylic acids, denotes 90 to 100 mol% of the p-phenylene groups, 0 to 7 mol% of the m-phenylene groups and 0 to 5 mol% of the aliphatic groups with 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms,
 X^1 , denotes the p-phenylene group,
 Y, in reference to the total amount of transesterified or esterified diols, denotes at least 90 mol% of the alkylene or polymethylene groups with 2 to 4 carbon atoms, or cycloalkane or dimethylene cycloalkane groups with 6 to 10 carbon atoms, and maximally 10 mol% of the straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8 carbon atoms, or groups of the formula $-(C_2H_4-O)_n-C_2H_4-$ in which n stands for the numbers 1 or 2.
10. A thermostable, color-neutral, antimony-free polyester based on aromatic dicarboxylic acids and aliphatic diols, producible by means of the method according to Claim 1, characterized by the fact that, in the unmatted state, among its color index components
 a^* lies in the range from -3 to +3,
 b^* lies in the range from -6 to +6 and
 L^* lies in the range from 55 to 75.
11. The thermostable, color-neutral, antimony-free polyester based on aromatic dicarboxylic acids and aliphatic diols according to Claim 10, characterized by the fact that it is antimony-free and contains
 1 to 10 ppm titanium,
 20 to 120 ppm of a transesterification catalyst metal in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or a derivative thereof,

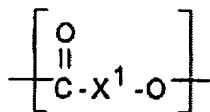
and 0 to 80 ppm of cobalt, which is partially present in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or a derivative thereof,
and optionally up to 50 ppm of an optical brightener.

12. The thermostable, color-neutral, antimony-free polyester according to at least one of the Claims 10 and 11, characterized by the fact that
it is antimony-free and contains
2 to 8 ppm of titanium,
50 to 90 ppm manganese (calculated as metal) in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or a derivative thereof,
20 to 40 ppm of cobalt, which is present partially in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or a derivative thereof, and
optionally up to 25 ppm of an optical brightener.
13. The thermostable, color-neutral, antimony-free polyester according to at least one of the Claims 10 to 12, characterized by the fact that, in the unmatted state, among its color index components
a* lies in the range from -2 to +2,
b* lies in the range from -3.5 to +3.5 and
L* lies in the range from 60 to 70.
14. The thermostable, color-neutral, antimony-free polyester according to at least one of the Claims 10 to 13, characterized by the fact that 90 to 99% of the cobalt is present in the form of catalytically inactive complexes with phosphoric acid, phosphorous acid and/or phosphonic acids or a derivative thereof.
15. The thermostable, color-neutral, antimony-free polyester according to at least one of the Claims 10 to 14, characterized by the fact that it contains 5 to 25 ppm of an optical brightener.
16. The thermostable, color-neutral, antimony-free polyester according to at least one of the Claims 10 to 15, characterized by the fact its polymer chains are constructed from 80 to 100 mol% of the structural groups of formula VI



(VI)

and 20 to 0 mol% of the structural groups of formula VII



(VII)

in which

X denotes more than 80 mol% of the aromatic groups with 5 to 16, preferably 6 to 12, carbon atoms and maximally 20 mol% of the aliphatic groups with 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms,

X¹ denotes the p-phenylene group,

Y denotes at least 80 mol% of the alkylene or polymethylene groups with 2 to 4 carbon atoms or cycloalkane or dimethylene cycloalkane groups with 6 to 10 carbon atoms and maximally 20 mol% of the straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8, carbon atoms or groups of the formula $-(\text{C}_2\text{H}_4-\text{O})_n-\text{C}_2\text{H}_4-$, in which n is a whole number from 1 to 40, in which case n = 1 or 2 is preferred for fractions up to 20 mol%, and groups with n = 10 to 40 are preferably present only in fractions of less than 5 mol%.

17. The thermostable, color-neutral, antimony-free polyester according to at least one of the Claims 10 to 16, characterized by the fact that it consists of structural groups of formula IV, in which

X denotes up to 90 to 100 mol% of the p-phenylene groups, 0 to 7 mol% of the m-phenylene groups and 0 to 5 mol% of the aliphatic groups with 4 to 10 carbon atoms, preferably 6 to 8 carbon atoms, and

Y denotes at least 90 mol% of the alkylene or polymethylene groups with 2 to 4 carbon atoms or cycloalkane or dimethylene cycloalkane groups with 6 to 10 carbon atoms and

- maximally 10 mol% of the straight-chain or branched alkanediyl with 4 to 16, preferably 4 to 8, carbon atoms or groups of the formula $-(C_2H_4-O)_n-C_2H_4-$, in which n stands for the numbers 1 or 2.
- 18. The thermostable, color-neutral, antimony-free polyester according to at least one of the Claims 10 to 17, characterized by the fact that it consists of structural groups of formula IV, in which
X denotes up to 93 to 99 mol% of the p-phenylene groups and 1 to 7 mol% of the m-phenylene groups.
- 19. The thermostable, color-neutral, antimony-free polyester according to at least one of the Claims 10 to 18, characterized by the fact that the catalytically inactive complexes of manganese and cobalt are complexes with phosphorous acid or an ester of the same.
- 20. The thermostable, color-neutral, antimony-free polyester according to at least one of the Claims 10 to 19, characterized by the fact that it optionally contains up to 1,000 ppm of crosslinking structural groups.

Fig.